# IONIC EXCHANGE REACTIONS OF COBALT AND OTHER FACTORS INFLUENCING THE ASSIMILATION OF COBALT BY RYEGRASS

BY

WILLIAM FRANKLIN SPENCER

B.S., University of Illinois, 1947
M.S., University of Illinois, 1950

## AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN AGRONOMY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

URBANA, ILLINOIS

1952

# IONIC EXCHANGE REACTIONS OF COBALT AND OTHER FACTORS INFLUENCING THE ASSIMILATION OF COBALT BY RYEGRASS

BY

WILLIAM FRANKLIN SPENCER

B.S., University of Illinois, 1947
M.S., University of Illinois, 1950

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN AGRONOMY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

URBANA, ILLINOIS

1952

## ACKNOWLEDGMENTS

The author appreciates the suggestions, criticisms, and encouragements of Dr. J. E. Gieseking under whose supervision this investigation was made. He is grateful to the Atomic Energy Commission for supplying the funds for the fellowship which he held during this investigation. He wishes to thank Dr. R. B. Duffield for furnishing the radioactive cobalt from an excess supply obtained for instructional purposes. He is grateful to the University of Illinois Chemistry Department for analytical equipment used throughout this study.

# IONIC EXCHANGE REACTIONS OF COBALT AND OTHER FACTORS INFLUENCING THE ASSIMILATION OF COBALT BY RYEGRASS

Cobalt is an essential element for animal nutrition, and its source is the plants on which animals feed. Rickes (1) and coworkers were the first to report that vitamin $B_{12}$ is a cobalt complex. A deficiency of cobalt was found to be responsible for the wasting disease (Enzootic Marasmus) of cattle and sheep. The plants consumed by the sick cattle and sheep were grown on soils low in cobalt.

Cobalt deficient areas have been reported in Michigan and Wisconsin and in several east coast states. A number of investigators have found that the total amount of cobalt in the soil does not indicate whether the plants grown on the soil will contain sufficient amounts of cobalt. The purpose of this investigation was to study some of the factors influencing the availability of the cobalt within the soil to plants.

The available soil cobalt is probably present in the adsorbed form. Cobalt is present in the soil in relatively small amounts; therefore, the adsorption and exchangeability of the cobalt ions at extremely low degrees of saturation become important. Analytical difficulties at these low cobalt concentrations were overcome by the use of radioactive cobalt as a tracer.

Wiklander and Gieseking (2) found that the exchangeability of an ion present on an exchanger in varying degrees of saturation is determined by its activity coefficient in relation to the activity coefficient of the complementary ion on the exchanger. As the degree of saturation of the exchanger by the ion is decreased, the exchangeability of the ion will increase, decrease, or remain constant depending upon the replacing power of the complementary ion relative to the replacing power of the ion in question. This principle was

utilized in the present investigation to ascertain the ease of release of the cobalt ion with respect to the calcium ion as the complementary ion on the exchanger. Exchange reactions were studied on a soil clay prepared from Swygert till, Wyoming bentonite, and Amberlite IR100 - a commercial cation exchanger. The exchangers were saturated to varying degrees with calcium and cobalt. Two symmetries of HCl were added and the amount of cobalt released was determined. The exchangeability of cobalt decreased slightly as the proportion of cobalt to calcium on the exchanger was decreased. This indicates that cobalt is harder to replace than calcium.

A study was made of the mechanism of the adsorption of the cobalt ion on the exchangers. Radioactive cobalt was added to samples of soil clays and Amberlite IR100, each saturated with calcium. The amounts of cobalt adsorbed, calcium released, and hydrogen ions formed in the reaction were determined. The results indicate that cobalt is adsorbed as the divalent cobaltous ion and as the monohydroxy cobaltous ion. The pH of the reaction medium presumably determines which ion predominates on the exchanger.

The mobility of cobalt in the soil was studied by observing the migration of radioactive cobalt placed in a column of soil. The $CaCO_3$ and water content of the soil column were varied. No significant differences in the movement of the cobalt were observed at the various $CaCO_3$ and water levels. An experiment was also carried out in a two compartment dialysis cell to ascertain the mobility of the cobalt ion. Soil containing cobalt was placed in one compartment of the cell and distilled water in the other compartment. The two compartments were separated by a Visking membrane. The amount of cobalt which diffused through the membrane was determined after 55 days. Less than 0.3 microgram of cobalt was found in the distilled water. Both migration studies indicate that cobalt is relatively immobile in the soil.

The effectiveness of HCl, $NH_4OH$, and acetic acid as extracting agents for soil-adsorbed cobalt was determined.

Radioactive cobalt was added to a series of soil samples one half of which had received $CaCO_3$ applications. The samples were left standing for two months after which they were boiled in the above named extracting agents. The HCl removed over 95 percent of the added cobalt, the acetic acid removed approximately 50 percent of the cobalt, and the $NH_4OH$ did not remove a measurable amount of the added cobalt. No significant differences were observed between the soils receiving $CaCO_3$ and the untreated soils.

Two crops of domestic ryegrass were grown in the greenhouse to study the uptake of radioactive cobalt at various pH levels. The amounts of cobalt applied were held constant while the pH was controlled by varying the amounts of lime applied to the soil. The first crop was grown with a constant low level of cobalt; whereas, the second crop was grown with a constant high level of cobalt. At the low cobalt level increasing amounts of cobalt were taken up by the plants as the lime application increased. At the high cobalt level more cobalt was taken up than at the low cobalt level but the amount did not vary directly with the lime application. Autoradiographs were taken of several of the grass plants in an attempt to determine the distribution of the cobalt within the plants. With immature plants no significant areas of concentration were observed. Autoradiographs of mature plants disclosed a relatively high concentration of radioactive cobalt in the nodes of the seed stalks.

## LITERATURE CITED

1. Rickes, E. L., Brink, N.G., Koniuszy, F. R., Wood, T. R., and Folkers, K. 1948. Vitamin $B_{12}$, a cobalt complex. Science 108:134.

2. Wiklander, L. and Gieseking, J.E. 1948. Exchangeability of adsorbed cations as influenced by the degree of saturation and the nature of the complementary ions with special reference to trace concentrations. Soil Science 66:377-384.

## VITA

The author was born March 4, 1923, in Carlinville, Illinois. He attended Dorchester grammar school and Carlinville Community High School where he graduated in June, 1940. After graduating from Blackburn College in June, 1942, he entered the University of Illinois. He was called into the army in 1943 and served in the American and Southwest Pacific theaters. Upon discharge from the army in 1946, he re-entered the University of Illinois. He received his Bachelor of Science degree in Agriculture with highest honors in June, 1947 and his Master of Science degree in Chemistry in August, 1950.

He was employed as Assistant in Soil Physics at the University of Illinois from June, 1948 to September, 1949. Since that time he has held an Atomic Energy Commission Predoctoral Fellowship in the biological sciences.

He is a member of Alpha Zeta, Gamma Sigma Delta, Sigma Xi, Phi Sigma, and Phi Kappa Phi.

## PUBLICATIONS

Spencer, W. F. and Gieseking, J. E. Organic Derivatives of Montmorillonite. Journal of Physical and Colloidal Chemistry. (in press)